

Development of an Electrochemical Acidification Cell for the Recovery of CO₂ and H₂ from Seawater II. Evaluation of the Cell by Natural Seawater

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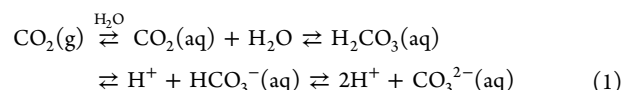
ABSTRACT: A novel electrochemical acidification process has been developed in a successful feasibility attempt to extract large quantities of CO₂ in the form of bicarbonate and carbonate from seawater for potential use as a source of carbon for hydrocarbon production at sea. This indirect approach acidifies seawater by the electrolytic production of acid. Lowering seawater pH was found to be proportional to the applied current to the cell. Spontaneous degassing and recovery of CO₂ below pH 4.5 was reduced from 92% in synthetic seawater to 30% in natural seawater. The effects of increased operational time, flow rate, current, and natural seawater's complex equilibrium buffer on process performance and CO₂ recovery have been shown to be essential for further improvements in future cell design, efficiency, and scale-up.

INTRODUCTION

Several electrochemical methods of chlorine dioxide production that involve both divided electrochemical cells and undivided cells have been reported.¹ Typically the divided cell process involves the separation of the anode and cathode compartment by a porous membrane that promotes ion transport while preventing mixing between compartments. In efforts to take advantage of the chlorine dioxide cell system commercial availability, versatility, size, and water capacity suitable for laboratory bench scale, a standard commercial chlorine dioxide cell was modified to simulate a cation exchange process with simultaneous electrolytic regeneration, or as an electrochemical acidification cell to control and manipulate seawater pH.² This novel hybrid process takes advantage of continuous electro-deionization (CEDI) principles of removing ionizable species from liquids by manipulating their ionic transport properties using an applied electrical potential, ion exchange resins, and semipermeable ion exchange membranes as electrically active media.^{3–8}

At seawater pH of less than or equal to 6, dissolved bicarbonate and carbonate re-equilibrate to CO₂ gas. This process has been the basis for standard quantitative ocean CO₂ measurements for over 25 years.⁹ The world's oceans contain approximately 100 mg of [CO₂]_T per liter of seawater.^{10,11} Approximately 2 to 3% of this CO₂ is in the dissolved gas form and the remaining 97 to 98% is chemically bound as bicarbonate (HCO₃[–]) and carbonate (CO₃^{2–}). The dissolved bicarbonate and carbonate are in equilibrium with dissolved carbonic acid species (eq 1) and it is these species that are primarily responsible for buffering and maintaining the ocean's

pH which is relatively constant below the top 100 m of depth.^{10,11}



On a w/v basis the total concentration of carbon dioxide [CO₂]_T in the ocean is approximately 140 times greater than in the air (0.7 mg/L) and on a w/w basis the concentration is 5.7 times higher than air (570 mg/kg).¹² If economic and efficient technologies could be developed to take advantage of the higher w/v concentration of CO₂ in seawater, future marine processes such as ocean thermal energy conversion (OTEC)^{13,14} and nuclear power¹⁵ could be envisioned to provide sufficient electrical power to utilize this carbon as a chemical feedstock in catalytic polymerization with hydrogen to produce value added hydrocarbons.¹⁶

Seawater's complex equilibrium buffer system (eq 1) and excessive salinity have presented unique challenges to developing technologies to capture large quantities of carbon dioxide and hydrogen from seawater. Gas-permeable membranes and simple strong base and strong acid ion-exchange resin systems were shown to be inefficient or impractical for CO₂ recovery from seawater.^{17–20} As one possible approach to take advantage of seawater pH, a commercial chlorine dioxide generation cell was reconfigured to function as an electro-

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chemical acidification cell.² Two cell configurations were evaluated using model synthetic seawater systems. Using these configurations, Willauer et al. showed the feasibility of extracting bound CO_2 in the ionic form of bicarbonate and carbonate in addition to the dissolved gas in solution.² The electrolytic production of acid to lower seawater pH was demonstrated and found to be proportional to the applied current to the cell and independent of the media contained in the center compartment. The CO_2 in the acidified seawater could be removed at pH less than 6 and the cell produced a portion of hydrogen gas through electrolytic reduction of water in the cathode compartment with no additional energy penalties.

Because the initial studies primarily focused on using synthetic seawater to determine the feasibility and best cell configuration for acidifying seawater,² this work was performed using natural seawater in order to simulate sample conditions that would be encountered in an actual ocean process for recovery of CO_2 . The effects of natural seawater's complex equilibrium buffer system, seawater flow rate, increased operational time, and current on seawater pH and CO_2 recovery were measured. These data are used to further evaluate the initial electrochemical cell design for future scale-up of the technology.

EXPERIMENTAL SECTION

A commercial Nalco chlorine dioxide generation cell (Nalco Company, Naperville, IL) was reconfigured to operate as an electrochemical acidification cell. Figure 1 shows the three-compartment cell configuration. The center compartment and the electrode compartments (cathode and anode) were separated by a Sybron MC-3470 reinforced/casted cation-permeable membrane. The acid functionality of the membranes provided discrete channels for Na^+ and H^+ ions to migrate

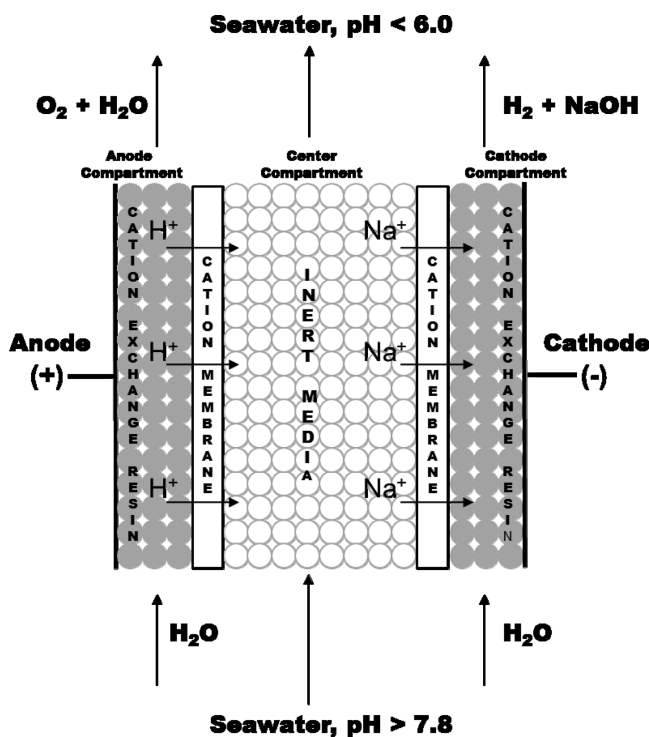


Figure 1. Electrochemical acidification cell. Positive ions travel through solution from anode to cathode→.

through the polymer matrix while blocking the passage of anions. The anode was a dimensionally stable anode (DSA) (mixed precious metal oxide coating on titanium), and the cathode was composed of 316 L stainless steel. The center compartment was filled with inert ceramic particles to serve as a support structure for the membranes. The electrode compartments were filled with strong cation exchange resin (Amberlite IRA-120 Rohm & Haas Company, Philadelphia, PA). A detailed description of the cell's electrical and flow rate specifications along with the materials used in the cell's configuration have previously been reported.²

Figure 2 is a schematic that describes the acidification experimental setup. Seawater was passed upwardly through the

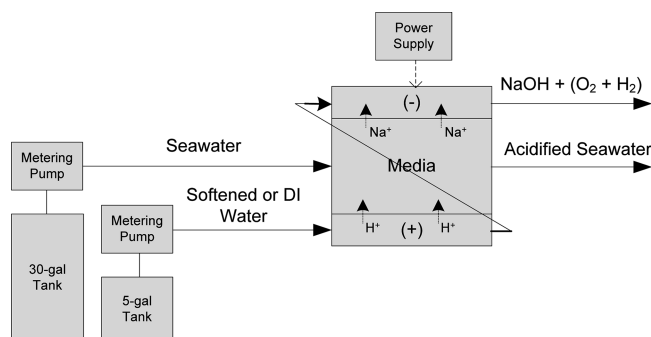


Figure 2. Schematic of electrochemical acidification experimental layout.

center compartment. Deionized water at a pH of approximately 6.7 and a conductivity less than $20 \mu\text{S}/\text{cm}$ was passed upwardly through the anode compartment and then upwardly through the cathode compartment in series. Deionized water was used as the anolyte because H^+ ions must be in surplus and not compete with any other cations. Deionized water was used as the catholyte fed to the cathode compartment because it must be free from hardness ions calcium (Ca^{2+}) and magnesium (Mg^{2+}) since the pH in the cathode compartment is high enough to precipitate these ions out of solution and onto the cathode surface. A controlled current between 0.4 and 1.2 A was applied across the anode and cathode in order to lower the pH of the seawater to a target level. This was a single pass system, so once a volume of seawater and deionized water passed through the cell it was not utilized again in the test.

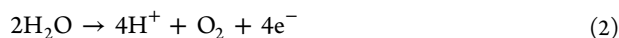
Natural Key West (KW) seawater was obtained from the Naval Research Laboratory Key West, Florida facility. The pH was 7.6 ± 0.2 and the $[\text{CO}_2]_{\text{T}}$ content was measured to be approximately 100 mg/L by coulometry. All coulometric measurements were made by a UIC Coulometric system (UIC Inc., Joliet, IL 60436).⁹ All pH measurements were conducted with a standardized Fisher combination glass electrode using certified calibration buffers 4, 7, 10 pH (Fischer Scientific, Pittsburgh PA).

Degassing measurements were made on selective samples during the course of the experiment. For each measurement the carbon dioxide was degassed from solution using a Brinkmann roto-evaporator. A 10 or 20 mL sample was placed in a 500 or 1000 mL round-bottom flask and rotated at an rpm setting of eight for 5 min. A water aspirator provided a vacuum of approximately 2 kPa (15 mmHg). The $[\text{CO}_2]_{\text{T}}$ content of the samples was measured by coulometry.

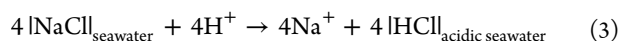
RESULTS AND DISCUSSION

Based on CEDI principles a novel hybrid electrochemical acidification process has been developed to acidify seawater as an indirect approach to recovering CO₂ from its bicarbonate form from the equilibrium conditions of CO₂ in seawater shown in eq 1. In the electrochemical process, depicted in Figure 1, H⁺ ions and O₂ gas were generated at the anode by the oxidation of the anolyte water. The O₂ gas is flushed from the anode compartment with the flow of the anolyte (deionized water). The H⁺ ions are driven from the surface of the anode, through the cation-permeable membrane, and into the center compartment where they replaced the Na⁺ in the flowing seawater. This caused the effluent seawater to be acidified. The Na⁺ ions were passed through the membrane closest to the cathode to produce primarily sodium hydroxide and H₂ gas in the cathode compartment. The NaOH and H₂ gas are continuously flushed from the cathode compartment with the flow of the catholyte (deionized water). The reactions within the electrochemical cell may be simplified as shown in eq 2–5 when sodium chloride (NaCl) is used to represent seawater and HCl is used to represent the acidified effluent seawater.

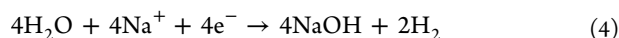
Anode:



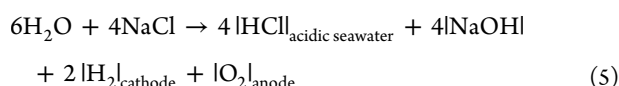
Center:



Cathode:



Overall:



The amount of H⁺ generated by the anode is proportional to the applied electrical current, which follows Faraday's constant. Faraday's constant is defined as the amount of electricity associated with one mole of unit charge or electron, having the value 96 487 ampere-second/equivalent.

For the anode reaction (eq 2), 96 487 A sec will produce 1/4 mol O₂ gas and 1 mol H⁺ and for the cathode reaction (eq 4), 96 487 A sec will produce 1/2 mol H₂ gas and 1 mol OH⁻. This allows the theoretical amount of H⁺, OH⁻, H₂, and O₂ produced per amp/second of current passed through the electrodes to be derived as follows:

Anode reaction:

$$\left(\frac{\frac{1}{4} \text{ mole O}_2}{96487 \text{ A} \cdot \text{sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.000155 \frac{\text{mole O}_2}{\text{A} \cdot \text{min}} \quad (6)$$

$$\left(\frac{1 \text{ mole H}^+}{96487 \text{ A} \cdot \text{sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.000622 \frac{\text{mole H}^+}{\text{A} \cdot \text{min}} \quad (7)$$

Cathode reaction:

$$\left(\frac{\frac{1}{2} \text{ mole H}_2}{96487 \text{ A} \cdot \text{sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.000311 \frac{\text{mole H}_2}{\text{A} \cdot \text{min}} \quad (8)$$

$$\left(\frac{1 \text{ mole OH}^-}{96487 \text{ A} \cdot \text{sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.000622 \frac{\text{mole OH}^-}{\text{A} \cdot \text{min}} \quad (9)$$

Therefore, seawater with a HCO₃⁻ concentration of 142 ppm (0.0023 M) and a flow rate of 1 L per minute will require a theoretical applied current of 3.70 A to lower the pH to less than 6.0 and convert HCO₃⁻ to H₂CO₃.

$$\frac{\left(\frac{0.0023 \text{ mole HCO}_3^-}{\text{liter}} \right) \left(\frac{1 \text{ liter}}{\text{min}} \right)}{\left(\frac{0.000622 \text{ mole H}^+}{\text{A} \cdot \text{min}} \right)} = 3.70 \text{ A} \quad (10)$$

The theoretical amount of CO₂ that can be removed from the acidified seawater is 0.0023 mols per liter. The theoretical amount of H₂ gas generated at 3.7 A is

$$\left(\frac{\frac{1}{2} \text{ mole H}_2}{96487 \text{ A} \cdot \text{sec}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) (3.70 \text{ A}) = 0.0011 \frac{\text{mole H}_2}{\text{min}} \quad (11)$$

Increasing the current increases the molar ratio of the measured hydrogen to carbon dioxide with no effect on the operation of the acidification cell. H⁺ generated will either exchange with Na⁺ in the seawater to further lower its pH or migrate through the center compartment and into the cathode compartment where it will combine with OH⁻ to form water.

In this test series the Nalco cell configuration was such that strong acid cation exchange resin filled the electrode compartments (Figure 1) and inert ceramic particles filled the center compartment. The electrochemical acidification cell was evaluated at two different sets of flow rate conditions.

In the first set of test conditions, Key West (KW) seawater passed through the center compartment at a flow rate of 140 mL/min and deionized water was passed through the electrode compartments at 10 mL/min. These test conditions were identical to those run previously to determine the initial feasibility of the approach.² Table 1 summarizes the results of

Table 1. Acidification of KW Seawater at an Influent Seawater Flow Rate of 140 mL/min and an Influent Deionized Water Flow Rate of 10 mL/min

time, min	amp/volt	flow rate to current ratio mL/(min-amp)	effluent acidified seawater pH
Initial Feasibility Studies II (1 st Test)			
15	0.47/4.81	298	6.11
30	0.48/4.79	292	7.07
45	0.52/4.84	269	6.96
60	0.58/5.11	241	7.01
75	0.69/5.57	203	6.59
90	1.00/6.73	140	6.04
105	1.25/7.51	112	5.22
120	1.14/6.91	123	4.66
135	0.94/6.22	149	4.96

the first test in the series. In the previous test series 0.47 A brought the seawater pH below 6. When the same current was applied to the cell in this test series, the pH of the effluent seawater was lowered from 7.8 to 6.11. As the current to the cell was increased further to 0.52, the pH of the effluent seawater unexpectedly increased. Table 1 shows that the pH of the effluent seawater remained above 6 as the current was increased from 0.47 to 1.0 A over a period of 90 min. After 105

min the pH fell to 5.22 at an applied current of 1.25 A. The pH was further reduced to 4.96 after 135 min at an applied current of 0.94, thus indicating less current was needed to lower the pH of the effluent seawater further. The flow rate to current ratio when the pH was lowered to 6.04 was estimated to be 140 mL/min/1.0 A = 140 mL/(min-amp) (Table 1). This ratio is significantly lower than the theoretical ratio of 267 calculated for similar conditions as described in eq 10 (3.7 A theoretical minimum) $1000 \text{ mL/min}/3.70 \text{ A} = 140 \text{ mL/min}/X$ and $X = 0.518 \text{ amps}$ so the theoretical ratio was $140 \text{ mL/min}/0.518 \text{ A} = 270 \text{ mL/(min-amp)}$. These results are inconsistent with the previous study in which the flow rate to current ratio when the seawater pH was lowered below 6 was 298 (140 mL/0.47 A).

The higher flow rate to current ratio in this test series may be explained by the equilibrium conditions of the ion exchange material in the cell's electrode compartments at the beginning of the test series. The cell had been stored in deionized water after the initial feasibility study for a period of six months. When the cell was first stored, the cation exchange resin was in the hydrogen form in the anode compartment and in the sodium form in the cathode compartment (Figure 1). During the six months of storage, the ions migrated within the cell. A portion of the cation exchange resin in the anode compartment converted to the sodium form while some of the cation exchange resin in the cathode compartment converted to the hydrogen form. Since the amount of H^+ ions generated from the oxidation of water on the anode is proportional to the applied electrical current, the higher current during the first 90 min of the test forced regeneration of the ion exchange material in the electrode compartments. The H^+ ions generated at the anode exchanged on the resin and released Na^+ ions. The Na^+ ions then migrated through the cation exchange membrane and into the center compartment. The migrating Na^+ ions passed through the cation exchange membrane at the cathode and exchanged on the resin to convert all the resin in that compartment to the sodium form. Table 1 suggests that after 90 min the ion exchange material in the electrode compartments was regenerated, allowing more H^+ ions to pass through the membrane closest to the anode to acidify the seawater. As a result, the current and pH of the effluent seawater dropped and the cell began functioning as anticipated. These results are important as they indicate the importance of re-establishing equilibrium conditions in the cell after prolonged periods in which the cell is not in operational use.

The first set of test conditions was repeated to verify the operational reproducibility of the cell. Table 2 shows that when 0.49 A of current were applied to the cell for 15 min, the pH of the effluent seawater was lowered from 7.70 to 5.62. The pH stabilized to 5.71 after an additional 15 min at the same applied current of 0.49 A. The flow rate to current ratio when the pH was 5.71 was estimated to be 286 (140 mL/min/0.49 A). This ratio is very similar to the theoretical ratio of 267 and consistent with the initial feasibility study in which the flow rate to current ratio when the seawater pH was lowered from 7.60 to 5.97 was 298 (140 mL/0.47 A) (Table 2).² As the current was increased further over 15 min intervals the pH of the effluent seawater continued to decrease. The test was conducted for a total of 105 min.

Figure 3 is a plot of the effluent acidified KW seawater pH as a function of applied current in amps for both feasibility studies shown in Table 2. The results in Figure 3 and Table 2 confirm that the cell was operating similarly to the previous test series once the ion exchange equilibrium conditions were re-

Table 2. Acidification of KW Seawater at an Influent Seawater Flow Rate of 140 mL/min and an Influent Deionized Water Flow Rate of 10 mL/min

time, min	amp/volt	flow rate to current ratio mL/(min-amp)	effluent acidified seawater pH
Initial Feasibility Studies II (2 nd Test)			
15	0.49/4.61	286	5.62
30	0.49/4.62	286	5.71
45	0.59/4.99	237	5.49
60	0.68/5.39	206	5.15
75	0.79/5.77	177	4.37
90	0.73/5.53	192	4.68
105	0.75/5.66	187	4.32
Initial Feasibility Studies I			
1	0.15/3.14	933	5.52
2	0.15/3.13	933	6.05
3	0.15/3.14	933	6.14
4	0.15/3.14	933	6.23
5	0.15/3.14	933	6.29
6	0.17/3.21	823	6.35
7	0.17/3.23	823	6.35
9	0.19/3.37	737	6.42
11	0.21/3.45	667	6.42
13	0.26/3.61	538	6.37
15	0.31/3.84	452	
17	0.40/4.06	350	6.20
19	0.47/4.33	298	6.09
21	0.47/4.34	298	6.04
23	0.47/4.33	298	5.97

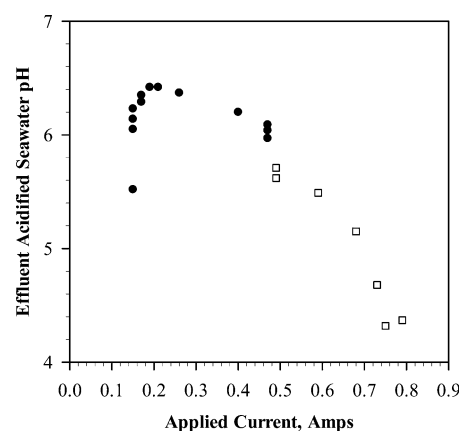


Figure 3. KW seawater acidification by electrochemical acidification cell: (●) Feasibility Test I and (□) Feasibility Test II.

established in the cell. The results demonstrate and confirm that lowering of the seawater pH was an electrically driven membrane process, where seawater pH was proportional to the applied current.

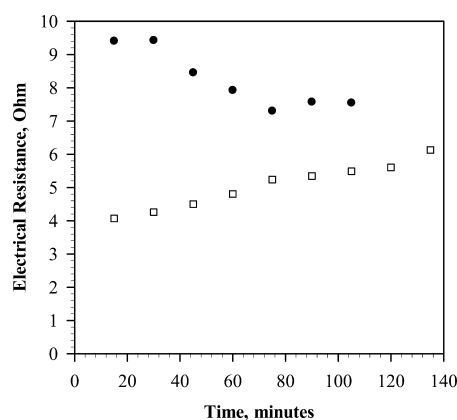
In the third test, KW seawater was used to determine the effect that flow rate through the center compartment had on the performance of the cell configuration. KW seawater was pumped at 700 mL/min and maintained for 135 min. The results summarized in Table 3 also include an additional test that was conducted for the purposes of collecting samples for degassing experiments. Table 3 confirms that at higher flow rates the pH of the effluent seawater can be lowered using the acidification cell. In addition, the results suggest that the flow rate to current ratio for a given pH under higher flow rate

Table 3. Acidification of KW Seawater at an Influent Seawater Flow Rate of 700 mL/min and an Influent Deionized Water Flow Rate of 50 mL/min

time, min	amp/volt	flow rate to current ratio mL/min-amp	effluent acidified seawater pH
Initial Feasibility Studies II (3 rd Tests)			
15	3.75/15.62	184	4.27
30	3.70/15.76	184	4.21
45	3.65/16.43	192	4.18
60	3.50/16.82	200	4.14
75	3.01/15.76	233	4.78
90	3.10/16.57	226	4.65
105	3.10/17.01	226	4.51
120	3.10/17.37	226	4.30
135	2.34/14.34	299	5.34
Degassing Experiments			
15	2.25/14.5	311	5.37

conditions was significantly improved and the recovery was at 93%. The term "recovery" is used to define the ratio of product quantity (influent seawater flow rate, Table 3) over the total feed quantity to the cell (influent seawater flow rate and influent deionized flow rate, Table 3) as a percent. This is critical since the water required in the electrode compartments must be dilute and free from hardness ions. This type of water must be pretreated by a filtration process such as reverse osmosis. A high recovery will allow the size of the filtration unit along with the energy requirements for the unit to be minimized in future scaled experiments.

Figure 4 is a plot of electrical resistance (voltage divide by amperage) as a function of time for the second and third tests.

**Figure 4.** Electrical resistance as a function of time for two different sets of electrochemical acidification cell flow rate conditions: (●) 140 and (□) 700 mL/min.

When the cell was operated at 140 mL/min of seawater to the center compartment, the electrical resistance initially decreased over time. After 75 min the Figure shows the electrical resistance began to increase slightly. This trend continued in the next test series as the KW seawater flow rate was increased from 140 to 700 mL/min. A 34% increase in the electrical resistance from 4.07 to 6.13 ohms over the course of the higher flow rate experiment was one of the signs of hardness scaling on the cathode. Scaling (mineral deposits) takes place at the high-pH surface of the cathode. The formation of mineral deposits increases the electrical resistance (voltage divided by amperage) of the cell leading to reduction in current efficiencies, and could

cause a pressure drop in the cathode compartment due to build-up of precipitate.

Since deionized water was the catholyte fed to the cathode compartment, hardness ions must have been introduced to the cathode from the center compartment. Hardness ions in seawater include calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, with a total concentration of less than 2000 mg/L. It was initially thought there would be a negligible likelihood of hardness ions migrating from the center compartment to the cathode compartment for the following reasons: First, the amount of cations that needed to be exchanged to lower the pH of the seawater was less than 0.5% of the total cations present in the seawater. Second, the molar ratio of Na^+ ions to Ca^{2+} and Mg^{2+} was approximately 7 to 1. Finally, the mobility coefficients of the ions favor Na^+ ($50.1 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$) over $1/2 \text{Ca}^{2+}$ ($59.5 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$) and $1/2 \text{Mg}^{2+}$ ($53.0 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$).

In future scaled experiments, the acidification cell will be designed so that the polarity of the cell can be reversed. Cyclically reversing the polarity of the cell's electrodes will reduce the mineral deposits, in the form of calcium and magnesium carbonate, on the electrode that is operating as the cathode. The change in polarity causes the minerals (scaling) to dissociate from the electrode surface. This is a common practice in the electrodialysis reversal (EDR) process to desalinate brackish ground and surface waters.⁴

In tests conducted using synthetic seawater at flow rates of 140 mL/min, greater than 98% of carbon dioxide in the seawater samples at a pH of less than 4.5 was spontaneously degassed upon exiting the acidification cell (exposed to atmosphere during sampling). When CO_2 is dissolved in seawater it is in equilibrium with H_2CO_3 as shown in eq 1. The hydration equilibrium constant (1.70×10^{-3}) indicates that H_2CO_3 is not stable and gaseous CO_2 readily dissociates at pH values below 4.5, allowing CO_2 to be easily removed by degassing. In efforts to substantiate this principle using natural seawater, effluent acidified seawater samples having a pH of 4.14 (Table 3) were collected and 20 mL aliquot solutions were measured before and after vacuum degassing by coulometry. The results are given in Table 4.

The initial $[\text{CO}_2]_T$ concentration of KW seawater was approximately 100 mg/L which corresponds to 0.0023 mol/L.

Table 4. CO_2 Degassed Samples from Acidification of KW Seawater at 700 mL/min

seawater	seawater (pH)	vacuum exposure time (min)	CO_2 Content (mg/L)	reduction (%)
initial seawater content	7.79	0	100	0
20 mL Samples				
effluent seawater table 3 time 60 min	4.14	0	70	30
effluent seawater Table 3 time 60 min	4.14	5	10	90
effluent seawater Table 3 flow rate conditions	5.37	5	21	79
10 mL Samples				
effluent seawater Table 3 flow rate conditions	5.37	5	1	99
effluent seawater Table 3 flow rate conditions	5.37	2.5	2	98
effluent seawater Table 3 flow rate conditions	5.37	1	2	98
effluent seawater Table 3 flow rate conditions	5.37	0.5	2	98

After the seawater solution was acidified to pH 4.1, the CO_2 content of the seawater measured 70 mg/L, thus indicating the solution was naturally degassed by 30% upon exiting the acidification cell (exposed to the atmosphere during sampling). When a vacuum was applied to an effluent sample for 5 min, the CO_2 content was reduced to 10 mg/L and 90% degassing was achieved.

The difference between the spontaneous degassing of CO_2 from natural seawater and synthetic seawater may be explained by the speciation diagram for CO_2 in seawater and CO_2 solubility. Figure 5 shows the relative portions of H_2CO_3 ,

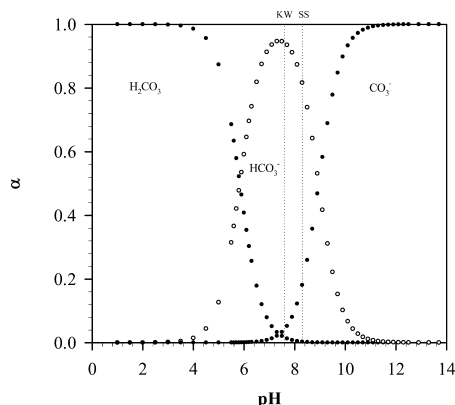


Figure 5. Relative seawater-carbonate species (H_2CO_3 , HCO_3^- , CO_3^{2-}) as a function of seawater pH at 25 °C, atmospheric pressure, and a seawater salinity of 35. The pH was measured for the natural Key West seawater (KW) and synthetic seawater (SW) studied.

HCO_3^- , and CO_3^{2-} species (eq 1) as a function of solution pH. The equilibrium constants for seawater vary as a function of temperature, pressure, and salinity causing shifts in the relative portions of each species of H_2CO_3 , HCO_3^- , and CO_3^{2-} . In Figure 5 the relative proportion of each species was calculated at atmospheric pressure, 25 °C, and a seawater salinity of 35 g/L.^{21,22}

The initial pH of the synthetic seawater and KW seawater used to originally evaluate the acidification cell was 8.3 ± 0.2 and 7.6, respectively. From Figure 5 the difference in pH between the two solutions indicates the ratio of carbonate ion was greater than 3.5 times higher in the synthetic seawater system.² In addition $[\text{CO}_2]_T$ measured only 10 mg/L. In efforts to create a synthetic formulation that had similar pH and alkalinity to KW, sodium bicarbonate was added to bring $[\text{CO}_2]_T$ to 100 mg/L and hydrochloric acid was used to adjust the pH from 8.3 ± 0.2 to 7.6 ± 0.2 . As a result, the CO_2 speciation of the newly formulated synthetic seawater was similar in nature to the natural seawater solution (Figure 5). However, the addition of Na^+ , H^+ , Cl^- , and HCO_3^- ions to the synthetic seawater solution not only changed the bicarbonate and carbonate equilibrium with dissolved CO_2 in the form of carbonic acid, but the overall CO_2 solubility in the solution. It is well-known that CO_2 gas solubility is reduced in aqueous salt solutions compared to deionized water solutions.^{23–25} As salt concentration increased with the introduction of Na^+ , H^+ , Cl^- , and HCO_3^- ions to the synthetic seawater, LeChatlier's Principle dictates equilibrium shift to the left (eq 1). The result is a decrease in CO_2 solubility that leads to the ease of spontaneous degassing of CO_2 from synthetic seawater compared to KW seawater.

The results of the previous test series using synthetic seawater also found that CO_2 in seawater samples having a pH less than 6.0 and greater than 4.5 required assistance by vacuum degassing for complete CO_2 removal. Preliminary studies to determine how pH effects vacuum degassing of CO_2 from natural seawater are shown in Table 4. After a 20 mL seawater sample having a pH of 5.37 was degassed for 5 min, 79% of the CO_2 content was removed. When the sample volume was reduced from 20 to 10 mL and the round-bottom flask from 1000 to 500 mL, a 99% removal of CO_2 was observed. When individual 10 mL effluent seawater samples were degassed over four different applied vacuum time intervals, complete degassing was measured for all four time intervals. These results confirm that at higher acidification seawater flow rates, the effluent KW seawater can be degassed at pH values lower than 6. However, the results indicate that under higher flow rate conditions sample volume and applied vacuum conditions may be extremely relevant to the future scaling of the system for purposes of efficiently producing large quantities of CO_2 as feedstock for synthetic jet fuel production.

CONCLUSIONS

An electrochemical acidification cell has been developed and tested as a function of seawater flow rate, increased operational time, and current on seawater pH and CO_2 recovery in natural KW seawater. KW seawater simulates sample conditions that will be encountered in an actual ocean process for recovering CO_2 . This indirect path captures bound CO_2 in the form of bicarbonate from seawater.

During the initial experiments sufficient current was needed to electrolytically regenerate the ion exchange materials in the cathode and anode compartments after the cell had been stored in deionized water for a period of six months. Once the ion exchange materials were regenerated within the acidification cell, the seawater pH was proportional to the applied current. Thus the results of KW seawater flow rates of 140 mL/min were consistent with the previous test series.² At higher seawater flow rates, the flow rate-to-current ratio for a given pH was significantly improved. However after prolonged operational times the electrical resistance increased by 34% signifying scaling on the cathode. The scaling resulted from the seawater hardness ions calcium (Ca^{2+}) and magnesium (Mg^{2+}) migrating from the center compartment.

Previous results found that at seawater pH values below 4.5, 92% of the $[\text{CO}_2]_T$ in synthetic seawater spontaneously degassed.² In contrast, this study found that at similar pH only 30% of the $[\text{CO}_2]_T$ was spontaneously degassed from natural KW seawater. The results may be explained by the carbonate/bicarbonate concentration of the synthetic seawater compared to natural KW seawater. In addition, results suggest that sample volume and applied vacuum conditions may be relevant as the acidification cell is scaled to handle higher seawater flow rate conditions in the future.

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Notes

The authors declare no competing financial interest.

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